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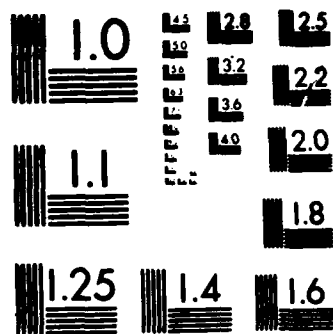   CHEMISTRY   G E WALRAFEN ET AL. 20 JUL 87 TR-20
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A plot of $E^2 - (\bar{E})^2$ (T,V,N) vs temperature from $-30°C$ to $150°C$ was found to be so nearly perfectly linear that small negative deviations near $-30°C$ suggested error in C_v rather than a failure of the linearity. An empirical equation was derived to describe C_v. Other properties of supercooled water were discussed.

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LIQUID

Fluctuations of Thermodynamic Properties of Super-Cooled Water

by

G. E. Walrafen and W. H. Yang

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FLUCTUATIONS OF THERMODYNAMIC PROPERTIES OF SUPERCOOLED LIQUID WATER

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It has been known for many years that fluctuations of several thermo-dynamic properties of supercooled liquid water are highly unusual. An example is the heat capacity at constant pressure, C_p. As water is supercooled, C_p rises very rapidly, particularly below about -20°C (Angell 1982). Because $\overline{S^2}-(\overline{S})^2 = k_B C_p$, where $k_B = 1.3806 \times 10^{-23}$ J°K^{-1}, it follows that the mean square fluctuations of the entropy, S, must *increase* as the temperature *decreases*. This situation is contrary to intuition, and immediately signals the presence of unusual effects, e.g., it suggests a continuous transformation between structures of markedly different entropy (Speedy 1984). Fluctuations of the enthalpy, energy, and molal volume, which *increase* with *decreasing* temperature at constant pressure (T,p,N ensemble) may be obtained from: $\overline{H^2}-(\overline{H})^2 = k_B T^2 C_p = k_B T^2[C_V+(\beta^2 TV/\kappa_T)]$, $\overline{E^2}-(\overline{E})^2 = k_B T\{TC_V + [(\partial E/\partial V)_T]^2\kappa_T V\}$, and $\overline{V^2}-(\overline{V})^2 = k_B T\kappa_T V$ (Kell 1982; Kubo 1981; McQuarrie 1976). (Temperature fluctuations, $\overline{T^2}-(\overline{T})^2 = k_B T^2/C_V$, increase at an increasing rate between -30°C and 150°C, and pressure fluctuations, $\overline{p^2}-(\overline{p})^2 = k_B T/V\kappa_S$, increase to a maximum near 100°C, and then decline with increasing temperature to 150°C.) $\beta = V^{-1}(\partial V/\partial T)_p$, $\kappa_T = -V^{-1}(\partial V/\partial p)_T$, $\kappa_S = -V^{-1}(\partial V/\partial p)_S = \kappa_T C_V/C_p$, and $(\partial E/\partial V)_T = p_i = (\beta T/\kappa_T)-p$.

Fluctuations corresponding to the canonical or T,V,N ensemble, for which V is fixed, are also of interest for liquid water. For this ensemble, $\overline{E^2}-(\overline{E})^2 = k_B T^2 C_V$ and $\overline{(E-\overline{E})^3} = k_B^2\{T^4(\partial C_V/\partial T)_V + 2T^3 C_V\}$ (Kubo 1981). $\overline{E^2}-(\overline{E})^2$ (T,V,N) is important because it constitutes the leading term in both $\overline{H^2}-(\overline{H})^2$ and $\overline{E^2}-(\overline{E})^2$ (T,p,N). Hence, $\overline{E^2}-(\overline{E})^2$ (T,V,N) may be regarded as a "baseline" above which $\overline{H^2}-(\overline{H})^2$ and $\overline{E^2}-(\overline{E})^2$ (T,p,N) (which are equal for practical purposes) both rise, below and above the temperature of minimum molal volume, 4°C.

A plot of $\overline{E^2}-(\overline{E})^2$ (T,V,N) *versus* temperature from -30°C to 150°C was found to be so nearly perfectly linear that small negative deviations near -30°C suggested error in C_V (determined from $C_p - \beta^2 TV/\kappa_T$), rather than a failure of the linearity. Therefore, if $\overline{E^2}-(\overline{E})^2 = a' + b'T$, it follows that $C_V T^2 = a + bT$, where b>0 and a<0. C_V values calculated between 0° and 100°C were considered to be more accurate than those over the remaining parts of the -30 to 150°C region. Least squares treatment (0° to 100°C) yielded the *empirical* relation, $C_V = -4,691,495T^{-2} + 37,930.92T^{-1}$, in J°k^{-1}mol^{-1}. ($C_p$ and C_V cannot be negative, but this is irrelevant for terms in an *empirical* equation.) To test the *empirical* equation values of $E_T-E_{277.16} = E_t-E_4$ were obtained from $C_V = C_p - (\beta^2 TV/\kappa_T)$ by graphi-cal integration *versus* the C_V values from the equation, obtained by analytical integration. The comparison is shown below. Some large deviations are seen to be 0.25% at -20°C, where C_p is given only to 3 significant figures (Angell 1982); and 0.1% at -30°C, where β is given only to 2 significant figures (Kell 1982).

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The third moment, $\overline{(E-\bar{E})^3}$, is readily calculated from $C_V = aT^{-2} + bT^{-1}$, namely $\overline{(E-\bar{E})^3} = bk_BT^2$. This moment is a measure of the skewness, which is relatively very small, as seen from $\overline{(E-\bar{E})^3}/\overline{E^2}-(\bar{E})^2 = bk_B/C_V = 6.92 \times 10^{-21}$, at 4°C.

Speedy (1984) has modelled the fluctuation $\overline{\Delta H \Delta V}$ in terms of pentagonal rings of hydrogen-bonded water molecules thought to exist in supercooled water. These rings are consistent with the presence of bulky polyhedral species. Speedy (1984) formulated $\overline{\Delta H \Delta V}$ as $k_B\beta T^2V$, which is the leading term in the formulation of Kubo (1981) $\overline{\Delta E \Delta V} = k_BT\{T\beta V-pV\kappa_T\}$. (H is nearly the same as E for liquid water.) In view of the present evidence that $\overline{S^2}-(\bar{S})^2$, $\overline{H^2}-(\bar{H})^2$, $\overline{E^2}-(\bar{E})^2$ and $\overline{V^2}-(\bar{V})^2$ all *increase* as the temperature of supercooled water *decreases*, it seems nearly certain that special, bulky, fully-hydrogen-bonded structures exist in highly supercooled water, where the molal volume rises sharply. Thus, these structures would be *volume modulated*, whereas the breakage of hydrogen bonds is *temperature modulated* (Walrafen 1986). Hence, these two modulation mechanisms *must be* considered for water.

Finally, one simple calculation highlights the great difference between supercooled water and ice at the same temperature. For supercooled water at -13°C, $(\partial E/\partial V)_T = p_i = -1900$ bar, whereas the corresponding p_i for ice ($\beta>0$ for ice, $\beta<0$ for water, -13°C) is about +3000 bar (Leadbetter 1965). This qualitative, large disparity of nearly 5000 bar emphasizes the differences between ice and super-cooled water. Large bulky polyhedral structures, *e.g.*, clathrate-type structures, do not exist in ice Ih, but such structures may exist in supercooled liquid water.

Table I.

t°C	$H_t - H_4$ *		$E_t - E_4$ *
	Graphical Integration		Analytical Integration
150	11077.88	10206.97	10210.46
140	10302.06	9569.56	9571.67
130	9534.60	8921.39	8923.96
120	8767.43	8266.10	8267.23
110	8003.55	7600.02	7601.41
100	7246.54	6925.71	6926.44
90	6487.21	6246.02	6242.28
80	5729.97	5552.24	5548.96
70	4974.30	4849.19	4846.54
60	4220.12	4137.46	4135.00
50	3468.93	3416.39	3414.93
40	2715.50	2684.79	2686.21
30	1962.43	1947.63	1949.39
20	1209.00	1203.12	1204.98
10	454.15	452.16	453.70
0	- 302.87	- 302.62	- 303.54
-10	-1067.04	-1062.99	-1065.55
-20	-1849.13	-1826.21	-1830.82
-30	-2677.27	-2594.45	-2597.39

* All figures carried here are not significant, *e.g.*, 4 significant figures are reasonable at most temperatures. Units, J/mol.

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